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[η^2-8-(*tert*-Butylimino)-1-naphthyl]bis(η^5-cyclopentadienyl)titanium(IV)

Huub Kooijman,[a]* Monique M. van Leijen,[b] Otto S. Akkerman,[b] Friedrich Bickelhaupt[b] and Anthony L. Spek[a]

[a]Bijvoet Centre for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and [b]Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Correspondence e-mail: h.kooijman@chem.uu.nl

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.056
wR factor = 0.131
Data-to-parameter ratio = 18.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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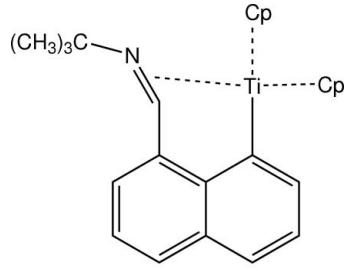
The title compound, $[Ti(C_5H_5)_2(C_{15}H_{15}N)]$, displays an iminoacyl fragment in an N-outside conformation, indicating that the C=N vector points away from the σ-bonded C atom. Considering only the geometrical centres of all η-coordinated groups, the Ti^{IV} ion adopts a severely distorted tetrahedral configuration. The crystal packing displays a short C—H$\cdots\pi$ contact linking the molecules into an infinite chain running along the *b*-axis direction.

Comment

The structure of the title compound, (I), was determined in the course of our investigations on the synthesis and reactivity of small metallacycles. A similar compound has been reported by Campora *et al.* (1995) and a related compound with Zr by Berg & Petersen (1989).



(I)

The structure of (I) is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. The title compound has two η^5-coordinated cyclopentadienyl (Cp) rings coordinated to the Ti^{IV} ion. The distances between the perpendicular projection of the Ti^{IV} ion on the Cp rings and their ring centroids (ring slippage) are 0.043 and 0.017 Å for the rings containing C16 and C21, respectively. The title compound further displays an iminoacyl fragment in an N-outside conformation, indicating that the C=N vector points away from the σ-bonded atom C2 (Tatsumi *et al.*., 1985). When the Cp rings and the C=N group are represented by their geometrical centres, as is suggested in Fig. 1, the Ti^{IV} ion displays a severely distorted tetrahedral configuration, with *X*—Ti—*Y* angles in the range 88.24 (11)–133.16 (9)° (Table 3). In an alternative description, the Ti^{IV} ion takes part in two adjacent titanacycles, the three-membered ring Ti1/C11/N11 and the five-membered ring Ti1/C2/C1/C10/C11. The maximum deviation from the least-squares plane through this last ring system is 0.028 (3) Å for C2. The Ti1—C2 bond is elongated by 0.2 Å compared with its parent compound 1,8-naphthalenediyltitanocene (Tinga *et al.*, 1994). The crystal packing displays a short C—H$\cdots\pi$ contact (Fig. 2 and Table 2),

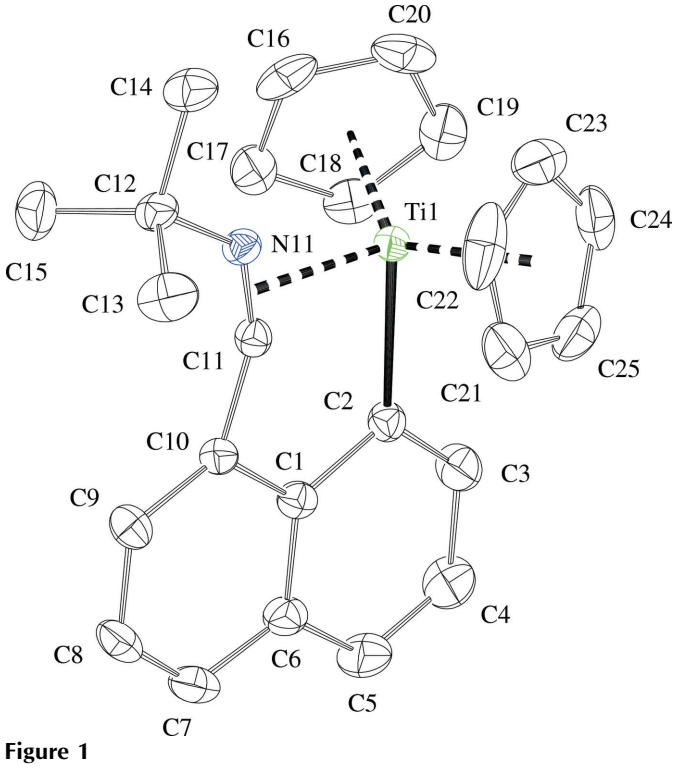


Figure 1
A view of the title compound, showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

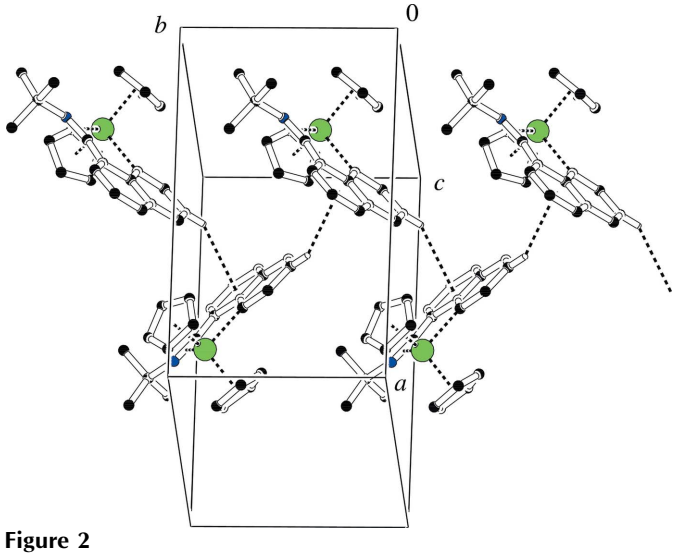


Figure 2
Section of the crystal packing illustrating the C4—H4···π interactions, viewed approximately perpendicular to the (10$\bar{2}$) planes. H atoms, with the exception of H4, have been omitted.

which links the molecules into an infinite chain running along the *b*-axis direction.

Experimental

A solution of 1,8-naphthalenediyltitanocene (0.1 mmol), prepared according to Tinga *et al.* (1994), in pentane (10 ml) was added to a solution of CN-^{t}Bu (0.2 mmol) in toluene (2 ml) at room temperature. After stirring for 3 h, the solvents were evaporated and the residue was extracted with cyclopentane. Brown crystals were obtained after a week from a solution in cyclopentane, which was kept at 280 K. Spectroscopic analysis: ^{1}H NMR (200 MHz, room temperature, C_6D_6, reference C_6D_5H = 7.17 p.p.m., p.p.m.): δ 7.85 (*m*, 1 H, H3), 7.83 (*m*, 1 H, H9), 7.68 (*m*, 1 H, H5), 7.58 (*m*, 1 H, H4), 7.50 (*m*, 1 H, H7), 7.37 (*m*, 1 H, H8), 5.20 (*s*, 10 H, 2Cp), 1.21 (*s*, 9 H, ^{t}Bu) (at 240 K a similar proton NMR spectrum was measured in CD_2Cl_2); ^{13}C NMR (50.3 MHz, room temperature, C_6D_6, reference C_6D_6 = 128.0 p.p.m., p.p.m.): δ 220.2 (*d*, ^3J = 3.3 Hz, C11), 191.2 (m, C2), 158.1 (*m*, C10), 140.3 (*ddd*, ^1J = 154.1 Hz, ^2J = 1.2 Hz, ^3J = 7.5 Hz, C3), 137.3 (*d*, ^3J = 7.6 Hz, C1 or C6), 135.0 (*dd*, ^3J = 8.0/6.6 Hz, C6 or C1), 132.0 (*d*, ^1J = 164.0 Hz, C9), 126.9 (*dd*, ^1J = 150.9 Hz; ^2J = 2.3 Hz, C4), 124.3 (*dd*, ^1J = 158.4 Hz, ^2J = 1.9 Hz, C8), 121.6 (*dd*, ^1J = 157.3 Hz, ^3J = 8.9 Hz, C7), 121.1 (*ddd*, ^1J = 157.3 Hz, ^3J = 9.4/8.2 Hz, C5), 105.5 (*dm*, ^1J = 171.0 Hz, 2Cp), 59.2 (*d*, ^2J = 4.2 Hz, C12), 29.3 (qsept, ^1J = 125.4 Hz, ^3J = 4.7 Hz, ^{t}Bu); IR (hexane) $\tilde{\nu}$ (cm^{-1}) 1726 (*s*); HRMS (EI) calculated for $C_{21}H_{16}N^{48}Ti$: 330.0764; found: 330.076; MS (EI) *m*/*z* (relative intensities): 387 (not observed, M^+), 330 (77, [M – ^{t}Bu]$^+$), 303 (17, [M – CHN-^{t}Bu]$^+$), 178 (38, Cp_2Ti^+), 128 (100, naphthalene, impurity).

Crystal data

$[Ti(C_5H_5)_2(C_{15}H_{15}N)]$
M_r = 387.33
Monoclinic, $P2_1/c$
a = 15.0891 (12) Å
b = 8.4475 (12) Å
c = 15.6025 (18) Å
β = 94.200 (13)°
V = 1983.4 (4) Å^3
Z = 4
D_x = 1.297 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.44 mm^{-1}
T = 298 K
Block, brown
0.5 × 0.4 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5661 measured reflections
4533 independent reflections
2344 reflections with $I > 2\sigma(I)$
R_{int} = 0.200
θ_{max} = 27.5°
3 standard reflections
frequency: 60 min
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.131
S = 1.00
4533 reflections
247 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ti1—N11	2.197 (3)	Ti1—C11	2.043 (3)
Ti1—C2	2.292 (3)	N11—C11	1.238 (4)
N11—Ti1—C2	104.45 (11)	C11—N11—C12	132.5 (3)
N11—Ti1—C11	33.70 (12)	N11—C11—C10	150.8 (3)
C2—Ti1—C11	70.75 (12)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···*Cg*4^{i}	0.93	2.98	3.768 (5)	143

Symmetry code: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$. *Cg*4 is the centroid of the C1/C6/C7/C8/C9/C10 ring.

Table 3
Tetrahedral geometry of Ti1 (angles in °).

*Cg*1 represents the centroid of the Cp ring C16–C20; *Cg*2 represents the centroid of the Cp ring C21–C25; *Cg*3 represents the mid-point of the N═C bond.

C2—Ti1—*Cg*1	103.22 (10)
C2—Ti1—*Cg*2	101.46 (11)
C2—Ti1—*Cg*3	88.24 (11)
*Cg*1—Ti1—*Cg*2	133.16 (9)
*Cg*1—Ti1—*Cg*3	110.35 (9)
*Cg*2—Ti1—*Cg*3	109.60 (10)

H atoms were introduced in calculated positions, with C—H = 0.93 and 0.96 Å, and refined as riding on their carrier atoms, with U_{iso}(H) = 1.5U_{eq}(methyl C) or 1.2U_{eq}(other C). The methyl groups were refined as rigid groups, allowing for rotation around the C—C bond.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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